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(71) Applicants *(for all designated States except US)*: DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). JAPAN SYNTHETIC RUBBER CO., LTD. [JP/JP]; 2-11-24, Tsukiji 2-chome, Chuo-Ku, Tokyo 104 (JP).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: KOMIYA, Zen [JP/JP]; 3-18-33, Umezono, Tsubuka City (JP). UKACHI, Takashi [JP/JP]; 5-22-9, Kamiya, Ibaraki, Ushiku 300-12 (JP).

(74) Agent: DEN HARTOG, Jeroen, Hendrikus, Joseph; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

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(54) Title: LIQUID CURABLE RESIN COMPOSITION

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(57) Abstract

A liquid curable resin composition comprising a urethane (meth)acrylate obtained by the reaction of a polyol, a diisocyanate, and a (meth)acrylate containing a hydroxyl group, and having a structural unit represented by formula (1). The composition has a low viscosity, exhibits excellent coatability, and produces cured product having superior durability and, particularly, free from coloration due to heat or lights. When used as a coating material for woods, plastic materials, and the like, the composition not only exhibits high productivity due to its excellent coatability, but also ensures coatings with prolonged durability.

LIQUID CURABLE RESIN COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a liquid curable resin composition producing cured products which are free from yellowing and excellent in durability.

Description of the Prior Art

In the production of optical fiber, a resin coating is provided for protection and reinforcement immediately after spinning molten glass fiber. A known structure of the resin coating consists of a primary coating layer of a flexible resin which is coated on the surface of optical fiber and a secondary coating layer of a rigid resin which is provided over the primary coating layer. A so-called optical fiber ribbon is known in the art in the application of optical fiber. The optical fiber ribbon is made from several such elemental optical fibers, e.g. four or eight optical fibers, by arranging these optical fibers in a plane and fixing them with a binder to produce a ribbon structure with a rectangular cross section. The resin composition for forming the primary coating is called a soft material; the resin composition for forming the secondary coating is called a hard material; and the binder for preparing the optical fiber ribbon from several elemental optical fibers is called a ribbon material.

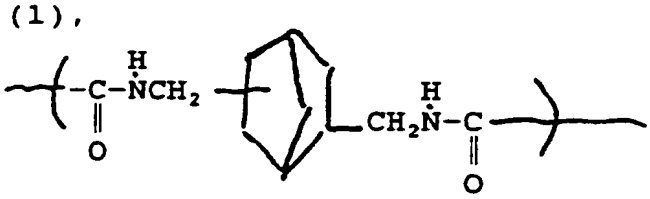
As laying of optical fiber cables develops in wide variety of environments in recent years, higher durability is demanded for coating materials of optical fiber, such as soft materials, hard materials, and ribbon materials. The characteristics required for curable resins used as the coating materials for optical fiber include: to be a liquid at ambient tem-

lights.

Another object of the present invention is to provide a liquid curable resin composition suitable as a coating material for optical fiber.

SUMMARY OF THE INVENTION

These objects of the present invention are achieved in the present invention by a liquid curable resin composition comprising a urethane (meth)acrylate obtained by the reaction of a polyol, a diisocyanate, and an acrylate containing a hydroxyl group, and having a structural unit represented by the following formula (1),



(1)

other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The structural unit of formula (1) possessed by the urethane (meth)acrylate used in the present invention can be derived from the diisocyanate of the following formula (2),

(2)

that is, from 2,5-bis(isocyanatemethyl)bicyclo[2.2.1]-heptane and/or 2,6-bis(isocyanatemethyl)bicyclo[2.2.1]-heptane, also called norbornene diisocyanate.

glycidyl ether, allylglycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidylbenzoate.

It is also possible to use a polyether diol obtained by the ring-opening copolymerization of the above-mentioned ionic polymerizable compounds and cyclic imines such as ethyl imine; cyclic lactones such as β-propiolactone and glycolic acid lactide; or cyclic siloxanes such as dimethylcyclopolysiloxane.

Specific examples of combinations of the two or more types of ionic-polymerizable cyclic compounds which can be given include tetrahydrofuran and propylene oxide; tetrahydrofuran and 2-methyltetrahydrofuran; tetrahydrofuran and 3-methyltetrahydrofuran; tetrahydrofuran and ethylene oxide; propylene oxide and ethylene oxide; butene-1 oxide and ethylene oxide; and ternary polymer of tetrahydrofuran, butene-1-oxide and ethylene oxide. The ring-opening copolymers of these ionic-polymerizable cyclic compounds may be bonded at random or in blocks.

Examples of these polyether diols which are commercially available include PTMG1000 and PTMG2000 (Mitsubishi Chemical Co., Ltd.); PPG1000, EXCENOL 2020, EXCENOL 1020 (Asahi Oline); PEGIOOO, UNISAFE DC1100, UNISAFE DC1800 (Nippon Oil and Fats Co., Ltd.); PPTG2000, PPTG1000, PTG400, PTGL2000 (Hodogaya Chemical Co., Ltd.); and Z-3001-4, Z-3001-5, PBG2000A, PBG2000B (Daiichi Kogyo Seiyaku Co., Ltd.).

Beside these polyether diols, polyester diols, polycarbonate diols, polycaprolactone diols, diols of a linear hydrocarbon, cyclic diols, and the like can be used as the diol compound in the present invention. These diols other than polyether diols can be used either independently or in combination with the

desirable for obtaining an adequate elasticity to use the linear hydrocarbon diols together with the polyether diol, polyester diol, or polycarbonate diol.

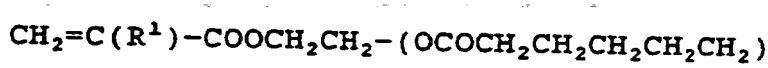
Included in the examples of the cyclic diols are 1,4-cyclohexane dimethanol, ethylene oxide addition diol to bisphenol A, butylene oxide addition diol to bisphenol A, ethylene oxide addition diol to bisphenol F, butylene oxide addition diol to bisphenol F, ethylene oxide addition diol to hydrogenated bisphenol A, butylene oxide addition diol to hydrogenated bisphenol A, ethylene oxide addition diol to hydrogenated bisphenol F, butylene oxide addition diol to hydrogenated bisphenol F, dimethylol compounds of dicyclopentadiene, and tricyclodecane dimethanol. Diols having a cyclic structure are preferably used when high elasticity of the products at high temperatures is required. Preferred diols having a cyclic structure among these compounds are ethylene oxide addition diol to bisphenol A and tricyclodecane dimethanol. These cyclic diols can be commercially available under the trademarks of DA400, DA700, DA1000 (Nippon Oil and Fats Co.), Tricyclodecanedimethanol (Mitsubishi Chemical Co.).

Other diol compounds may be used either independently or in combination with the diols mentioned above. Given as examples of such other diols are β-methyl-δ-valerolactone, polybutadiene with hydroxyl terminal groups, hydrogenated polybutadiene with hydroxyl terminal groups, castor oil-denatured diol, polydimethylsiloxane with terminal diols, and polydimethylsiloxane carbitol-denatured diols.

As the triols, trimethylolpropane, ethylene oxide adducts of trimethylolpropane, propylene oxide adducts of trimethylolpropane, butylene oxide adducts of trimethylolpropane, glycerine, ethylene oxide adducts of glycerine, propylene oxide adducts of glycerine, and butylene oxide adducts of glycerine can

The amount of these diisocyanates other than the diisocyanates of formula (2) is preferably about 50% by weight or smaller of the total amount of diisocyanates. If more than about 50% by weight, the effects of the low viscosity and high durability may be decreased.

Examples of a (meth)acrylate having a hydroxyl group used in the present invention include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl(meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, (meth)acrylates represented by the following structural formulas (3) or (4),



(3)

(4)

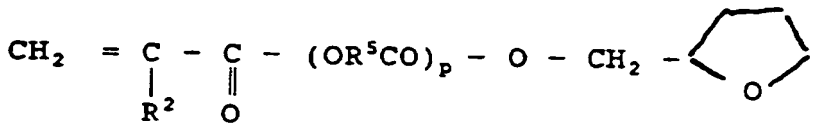
wherein R^1 is a hydrogen atom or a methyl group and n denotes an integer of 1-15. In addition, compounds obtained by an addition reaction between a compound containing a glycidyl group, such as, alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid can also be used.

Among these (meth)acrylates having a hydroxyl group, particularly desirable are 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate.

The polyol, the diisocyanate, and the (meth)acrylate containing a hydroxyl group are used preferably in a proportion such that about 1.1-3

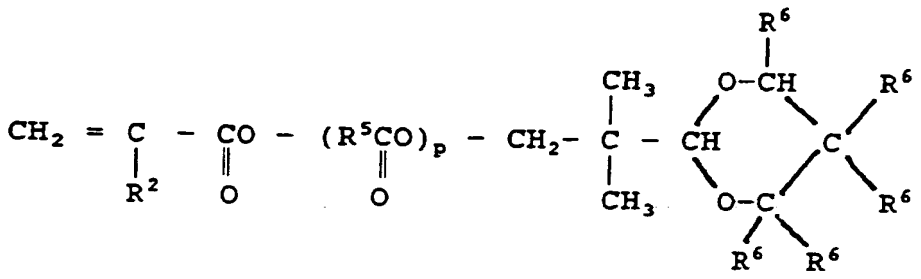
Besides these components, a urethane di(meth)acrylate, which can be obtained by reacting two mols of urethane (meth)acrylate containing a hydroxyl group with one mol of diisocyanate, can be incorporated to the liquid curable resin composition of the present invention. Given as examples of such a urethane di(meth)acrylate are the reaction product of hydroxyethyl (meth)acrylate and the diol of the formula (2), the reaction product of hydroxyethyl (meth)acrylate and 2,4-tolylene diisocyanate, the reaction product of hydroxyethyl (meth)acrylate and isophorone diisocyanate, the reaction product of hydroxypropyl (meth)acrylate and 2,4-tolylene diisocyanate, and the reaction product of hydroxypropyl (meth)acrylate and isophorone diisocyanate. These urethane di(meth)acrylate may be added in an amount of smaller than 30% by weight of the total amount of the composition.

Polymerizable monofunctional vinyl monomers or polymerizable polyfunctional monomers can be added to the urethane (meth)acrylate of the liquid curable resin composition of the present invention. Examples of the polymerizable monofunctional vinyl monomers include lactams containing a vinyl group, such as N-vinyl pyrrolidone and N-vinyl caprolactam; alicyclic (meth)acrylates, such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, and cyclohexyl (meth)acrylate; benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate; (meth)acryloyl morpholine, vinyl imidazole, and vinyl pyridine. Other examples of the monofunctional compounds are 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl



(6)

wherein R^2 is the same as defined above; R^5 is an alkylene group containing 2 to 8, preferably 2 to 5, carbon atoms; and p is an integer from 1 to 8, and preferably from 1 to 4.



(7)

wherein R^2, R^5, and p are the same as defined above; and R^6s are individually a hydrogen atom or a methyl group. Commercially available monofunctional compounds include ARONIX M111, M113, M114, M117 (Toagosei Chemical Industry Co., Ltd.), KAYARAD DTC110S, R629, R644 (Nippon Kayaku Co., Ltd.), and Viscoat 3700 (Osaka Organic Chemical Industry, Ltd.).

Examples of the polyfunctional compounds include: trimethylolpropane tri(meth)acrylate, pentaerythritol (meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycoldi(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxyethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, and di(meth)acrylate of a diol which is an ethylene oxide or propylene oxide adduct to bisphenol A, di(meth)acrylate of a diol which is an ethylene oxide

composition of the present invention is cured with lights, a photo-polymerization initiator, optionally in combination with a photosensitizer, is preferably used. Examples of the photo-polymerization initiator include 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyll-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide; and commercially available products, such as Irgacure 184, 369, 651, 500, 907 CGI1700, CGI1750, CGI1850, CG24-61 (Ciba Geigy), Lucirin LR8728 (BASF), Darocure 1116, 1173 (Merck Co.), and Uvecryl P36 (UCB).

Given as examples of the photo-sensitizers are triethylamine, diethylamine, N-methyldiethanolamine, ethanolamine, 4-dimethylaminobenzoic acid, methyl 4-dimethyl-aminobenzoate, ethyl 4-dimethyl-aminobenzoate, isoamyl 4-dimethylaminobenzoate, and commercially available products such as Uvecryl P102, P103, P104, and P105 (manufactured by UCB Co.). When the liquid curable resin composition of the present invention is cured using heat and UV lights together, the photo-polymerization initiator and the heat-polymerization initiator can be used in combination. These polymerization initiators are incorporated in the composition in an amount of about 0.1-10% by weight, and preferably about 0.5-7% by weight.

Beside the above components, the liquid

composition of the present invention is normally in the range of about 200 to about 20,000 dPa.s at 25°C, and preferably about 2,000 to about 15,000 dPa.s at 25°C. When the composition is used as a ribbon material or secondary coating for optical fiber, the Young's modulus of the composition after it has been cured is normally about 10-250 kg/mm^2, and preferably about 40-150 kg/mm^2. When used as a primary coating for optical fibers, the cured product preferably has a Young's modulus of about 0.05-0.3 kg/mm^2.

The liquid curable resin composition of the present invention is cured by heat and/or radiation. Here, the radiation means radiations such as infrared lights, visible lights, ultraviolet lights, X-rays, electron beams, α-rays, β-rays, and γ-rays.

The present invention will be hereinafter described in more detail by way of examples which are given for illustration of the present invention and shall not to be construed as limiting the present invention. In the examples hereinafter "part(s) by weight" is simply described as "part(s)".

EXAMPLES

Preparation of urethane acrylate (1)

3.6 parts of a 50:50 (by weight) mixture of 2,5-bis(isocyanatemethyl)bicyclo[2.2.1]heptane and 2,6-bis(isocyanatemethyl)bicyclo[2.2.1]heptane (hereinafter called NBDI), 50.5 parts of a ring-opening copolymer of ethylene oxide and butene oxide having a number average molecular weight of 4,000, and 0.01 part of 2,6-di-tert-butyl-p-cresol, as a polymerization inhibitor, were placed in a reaction vessel equipped with a stirrer. While stirring, the mixture was cooled with ice to below 10°C, whereupon 0.04 part of dibutyltin dilaurate was added. The mixture was stirred for 2 hours while controlling the temperature at 20-30°C.

temperature at 20-30°C. After the addition of 2.2 parts of hydroxyethyl acrylate, the mixture was stirred for a further 4 hours at 50-60°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. The liquid of the urethane acrylate resin thus obtained is referred to as UA-3.

Examples 1-8

<Preparation of liquid curable resin compositions>

Liquid compositions for coating as the upper layer of optical fibers were prepared from the components shown in Table 1, by charging these components to a reaction vessel equipped with a stirrer and stirring the mixture for 3 hours at 50-60°C.

Footnote for Table 1 (continued)

LA: Lauryl acrylate, a polymerizable monomer manufactured by Kyoeisha Chemical Co.

BAPO: Bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, a photo-polymerization initiator

Lucirin: 2,4,6-Trimethylbenzoyldiphenylphosphine oxide, a photo-polymerization initiator manufactured by BASF

Irganox 1035: Antioxidant manufactured by Ciba-Geigy

Preparation of urethane acrylate (4)

19.5 parts of NBDI, 0.06 part of dibutyltin dilaurate, 0.015 part of 2,6-di-tert-butyl-p-cresol, and 11.9 parts of tricyclodecanedimethanol diacrylate were placed in a reaction vessel equipped with a stirrer and cooled to 15°C or lower. 15.25 parts of hydroxyethyl acrylate was added dropwise while stirring and controlling the temperature at 30°C or lower. After the addition, the mixture was reacted for 1 hour at 30°C. Then, 2.64 parts of tricyclodecanedimethanol and 28.5 parts of a ringopening copolymer of tetrahydrofuran and 3-methyltetrahydrofuran having a number average molecular weight of 2,000 were added and the mixture was stirred at 20-55°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. To the resulting reaction mixture were added 7.95 parts of N-vinylpyrrolidone, 6.74 parts of isobornyl acrylate, 3.45 parts of tricyclodecane-dimethanol diacrylate, 0.3 part of Irgacure 1035 (manufactured by Ciba Geigy), and 0.14 part of 2,6-di-tert-butyl-p-cresol, and the mixture was stirred while controlling the temperature at 50-60°C until a homogeneous, transparent liquid was obtained. This transparent liquid of urethane acrylate resin is referred to as UA-4.

Examples 9-12

<Preparation of liquid curable resin compositions>

Liquid compositions for coating secondary, upper layer were prepared from the components shown in Table 2, by charging these components to a reaction vessel equipped with a stirrer and stirring the mixture for 3 hours at 50-60°C.

TABLE 2

Component	Example 9	Example 10	Example 11	Example 12
UA-4	97	0	98	0
UA-6	0	97	0	98
Irgacure 184	3	3	0	0
Lucirin	0	0	1.5	1.5
Irgacure 907	0	0	0.5	0.5

Irgacure 184: 1-Hydroxycyclohexyl phenyl ketone (a photo-polymerization initiator)

Irgacure 907: 2-Methyl-1-[4-(methylthio)phenyl]-2-molphorinopropane-1-one (a photo-polymerization initiator)

Lucirin: A photo-polymerization initiator

Preparation of urethane acrylate (7)

3.0 parts of tolylene diisocyanate, 50.5 parts of a ring-opening copolymer of ethylene oxide and butene oxide having a number average molecular weight of 4,000, and 0.01 part of 2,6-di-tert-butyl-p-cresol, as a polymerization inhibitor, were placed in a reaction vessel equipped with a stirrer, cooled with ice to below 10°C while stirring. At the temperature of below 10°C, 0.04 part of dibutyltin dilaurate was added and the mixture was stirred for 2 hours while controlling the temperature at 20-30°C. Then, 0.3 part of γ-mercaptopropyltrimethoxy silane was added,

TABLE 3

Component	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
UA-7	55	55	0	0
UA-8	0	0	50	50
M113	15	15	20	20
M114	0	17	0	0
IBXA	21	0	14	14
Vcap	6	3	6	6
LA	0	7	7	7
Lucirin	1.5	0	1.5	1.5
BAPO	0	1.5	0	0

In Table 3, M113, M114, IBXA, Vcap, LA, BAPO, and Lucirin are the same as defined for Table 1.

Preparation of urethane acrylate (9)

16.5 parts of toluene diisocyanate, 0.06 part of dibutyltin dilaurate, 0.01 part of 2,6-di-tert-butyl-pcresol, and 11.9 parts of tricyclodecanedimethanol diacrylate were placed in a reaction vessel equipped with a stirrer and cooled to below 15°C. Then, 15.25 parts of hydroxyethyl acrylate was added dropwise while stirring to control the temperature at 30°C or lower. After the addition, the mixture was reacted for 1 hour at 30°C. Then, 2.64 parts of tricyclodecane dimethanol and 28.5 parts of a ring-opening copolymer of tetrahydrofuran and 3-methyltetrahydrofuran having a number average molecular weight of 2,000 were added and the mixture was reacted at 20-55°C until the amount of residual isocyanate was below 0.1% by weight, whereupon the reaction was terminated. To the resulting reaction mixture were added 7.95 parts of N-vinylpyrrolidone, 6.74 parts of isobornyl acrylate, 3.45 parts of tricyclodecanedimethanol diacrylate, 0.3 part of Irganox 1035 (manufactured by Ciba Geigy), and 0.14 part of 2,6-di-tert-butyl-p-cresol, and the mixture was stirred while controlling the temperature at 50-60°C

Ciba Geigy), 50.3 parts of UA-10, and 0.3 part of diethylamine, followed by stirring at 40-50°C to obtain a homogeneous, transparent liquid. This transparent liquid of urethane acrylate resin is referred to as UA-11.

Comparative Examples 5-8

<Preparation of comparative liquid curable resin compositions>

Liquid compositions for coating secondary, upper layer were prepared from the components shown in Table 4, by charging these components to a reaction vessel equipped with a stirrer and stirring the mixture for 3 hours at 50-60°C.

TABLE 4

Component	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
UA-9	97	0	98	0
UA-11	0	97	0	98
Irgacure 184	3	3	0	0
Lucirin	0	0	1.5	1.5
Irgacure 907	0	0	0.5	0.5

In Table 4, Irgacure 184, Lucirin, and Irgacure 907 are the same as defined for Table 2.

Test Examples

The liquid curable resin compositions prepared in the above examples were cured and test leaves were prepared from the resin by the method mentioned below. The following tests were carried out to evaluate the test leaves.

(i) Preparation of test leaves

The liquid curable resin compositions were coated on glass plates using an applicator bar with a thickness of 250 μm. The coating was irradiated by UV light at 1 j/cm^2 in the air. The cured films as they

TABLE 5

	Example 1		Example 2		Example 3		Example 4		Example 5		Example 6	
	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI
Initial Value	1.2	1.8	1.3	1.9	1.1	1.8	1.0	1.3	1.5	1.6	1.3	1.7
QUV (after 7 days)	1.4	2.7	1.5	2.6	1.3	2.7	1.5	2.1	1.9	2.8	1.5	2.0
120°C (after 14 days)	8.5	14.1	9.4	15.2	8.4	13.4	7.3	14.1	10.1	16.3	7.6	12.9
Viscosity (dPa.s at 25°C)	3000		2300		2200		3200		3800		3000	

TABLE 6

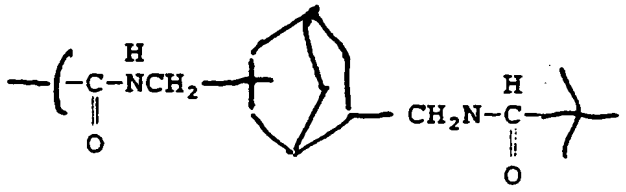
	Example 7		Example 8		Example 9		Example 10		Example 11		Example 12	
	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI
Initial Value	1.3	1.6	1.5	1.9	1.4	1.6	1.5	1.8	1.3	1.5	1.0	1.3
QUV (after 7 days)	1.6	2.4	1.6	2.8	1.9	3.0	2.1	3.3	2.0	2.7	1.8	2.5
120°C (after 14 days)	8.4	13.6	9.4	17.5	9.5	18.1	8.3	19.0	7.9	16.3	9.1	16.1
Viscosity (dPa.s at 25°C)	3800		3300		3200		4000		3300		4000	

TABLE 7

	Comparative Example 1		Comparative Example 2		Comparative Example 3		Comparative Example 4		Comparative Example 5		Comparative Example 6	
	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI
Initial Value	1.2	1.8	1.3	1.8	1.0	1.6	1.3	1.6	1.5	1.8	1.3	1.9
QUV (after 7 days)	11.0	19.1	12.5	20.4	11.9	21.3	12.0	17.4	14.4	21.3	12.1	23.1
120°C (after 14 days)	13.5	19.5	13.8	20.1	15.6	23.4	14.0	18.5	15.6	20.8	14.5	23.8
Viscosity (dPa.s at 25°C)	9000		8500		8500		8300		7900		7900	

WHAT IS CLAIMED IS

1. A liquid curable resin composition comprising a urethane (meth)acrylate obtained by the reaction of a polyol, a diisocyanate, and a (meth)acrylate containing a hydroxyl group, and having a structural unit represented by the following formula (1),



(1)

2. The liquid curable resin composition according to claim 1, wherein the diisocyanate is 2,5-bis(isocyanatemethyl)bicyclo[2.2.1]heptane and/or 2,6-bis(isocyanatemethyl)bicyclo[2.2.1]heptane, or a combination of these diisocyanate and other organic diisocyanate.

3. The liquid curable resin composition according to any one of claims 1-2, wherein the urethane (meth)acrylate has a number average molecular weight of about 500-15,000.

4. The liquid curable resin composition according to any one of claims 1-3, containing about 10-90% by weight of the urethane (meth)acrylate.

5. The liquid curable resin composition according to any one of claims 1-4, further containing a urethane (meth)acrylate which is a reaction product of one mol of a diisocyanate and two mols of a (meth) acrylate containing a hydroxyl group.

6. The liquid curable resin composition according to any one of claims 1-5, further containing a polymerizable monofunctional vinyl monomer.

7. The liquid curable resin compound according to any one of claims 1-6, further containing a

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/NL 96/00404

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/81 C08G18/75 C08G18/67 C08F299/06 G02B6/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C08F G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9427 Derwent Publications Ltd., London, GB; Class A89, AN 94-221869 XP002021926 & JP,A,06 157 451 (MITSUI TOATSU CHEM INC) , 3 June 1994	1,2
Y	- see abstract ---	3-10
Y	DATABASE WPI Section Ch, Week 8222 Derwent Publications Ltd., London, GB; Class A25, AN 82-44876E XP002021927 & JP,A,57 067 622 (TOYODA GOSEI KK) , 24 April 1982 see abstract --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 January 1997	11. 02. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Heidenhain, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. onal Application No
PCT/NL 96/00404

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-4126860	18-02-93	NONE	
EP-A-0168173	15-01-86	CA-A- 1237233	24-05-88
		JP-B- 7074259	09-08-95
		JP-A- 61004719	10-01-86
		JP-A- 7206975	08-08-95
		US-A- 4607084	19-08-86